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(54) PROCESS FOR THE PREPARATION OF POLYPROPENE COMPOSITIONS IN THE FORM OF A POWDER WHICH CAN BE PROCESSED INTO PRODUCTS OF IMPROVED FALLING-WEIGHT IMPACT STRENGTH

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. formerly known as Shell Internationale Research Maatschappij N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The invention relates to a process for the preparation of polypropene compositions in the form of a powder which can be processed into products of improved falling-weight impact strength and which contain a predominantly isotactic propene polymer (polymer A) and a rubberlike ethene-propene copolymer (polymer B), which may or may not be bound to polymer A, by the following procedure, to be carried out in the presence of a liquid diluent:

- (a) polymerizing propene to a suspension of polymer A;
 - (b) copolymerizing ethene and propene to a suspension containing polymer B, and;
 - (c) mixing the polymers A and B during or after the copolymerization mentioned under (b);
- and subsequently removing the diluent from the final suspension thus obtained.

By a "predominantly isotactic propene polymer" is understood a propene polymer of which more than 50 per cent is crystallizable and cannot be extracted with n-heptane. In the first place predominantly isotactic homopolymers of propene are meant, but also predominantly isotactic propene polymers obtained by conducting the polymerization of propene in the presence of at most 5 and pre-

ferably less than 2 per cent by weight of ethene can act as polymer A according to the present invention.

In the composition to be prepared the polymers A and B may be present as separate, non-bound polymers. However, the two polymers may also be partly bound together. The latter situation may occur, for instance, when polymer B is prepared in the presence of polymer A which contains still-active catalyst.

According to the invention polypropene compositions in the form of a powder of the type described are obtained, which furthermore show little or no tendency to stick, in other words have good powder flow properties, if in the preparation each of the following five requirements is fulfilled:

- (1) the polymerization of propene to a suspension of polymer A must take place with the aid of a catalyst system consisting of an organo-metallic component C and a component D which has been prepared beforehand by mixing, in a liquid paraffinic diluent and with stirring, $\text{Al(alkyl)}_2\text{Cl}$ and TiCl_4 at a temperature below -5°C ., preferably between -5 and -45°C ., in particular between -10 and -40°C ., and in a molar ratio of 0.5—1.2, preferably of 0.65—1.00, in which process the beta-modification of TiCl_4 is formed, and subsequently raising the temperature of the mixture thus obtained to 70 — 200°C ., with continued stirring (whereby the beta- TiCl_4 is converted into the gamma-modification);
- (2) the intrinsic viscosity of polymer A, measured in decalin at 135°C ., must be 1—4.5 dl/g;
- (3) polymer B must contain 20—90 per cent by weight, preferably 40—70 per cent by

- weight, of copolymerized ethene, a percentage by weight of ethene of 50—65 being preferred in particular;
- (4) in the final suspension the weight ratio between polymer B and the sum of polymer A and polymer B must be 0.08—0.20, preferably 0.11—0.18, the most preferred ratio being 0.11—0.15; and
- (5) the melt index of the final mixture of polymer A and polymer B must be between 0.1 and 15.0, measured at 230° C. according to British Standard 2782, Part I.

By employing the catalyst system described under (1) it is easy to obtain suspensions of polymer A that have a polymer concentration of 25—35 per cent by weight and that can still be stirred very well. This is an important advantage of the present process. Therefore, in the preparation of the suspension of polymer A the polymerization is preferably continued until a polymer concentration of more than 25 per cent by weight is reached, a polymer concentration of 30—37 per cent by weight in the final suspension, before removal of the diluent, being preferred.

The polymer B/polymer A+polymer B weight ratio of 0.08—0.20 is preferably realized by carrying out the preparation of polymer B in the presence of a polymer-A suspension which contains still-active catalyst. Such a process can very suitably be carried out by performing the polymerization to polymer A and the copolymerization to polymer B continuously in separate reactors, the suspension obtained at the end of the preparation of polymer A—which suspension contains still-active catalyst—being fed to the reactor in which polymer B is prepared. In this case no fresh supply of catalyst need be added in the latter reactor.

However, it is also possible to prepare polymer B in the absence of polymer A and subsequently mixing the suspensions of polymer A and polymer B. The catalyst system which is then used in the preparation of polymer B may be identical to or differ from that employed in the preparation of polymer A. This process, too, can be carried out continuously.

In the preparation of catalyst component D the mixing of the $\text{Al(alkyl)}_2\text{Cl}$ and the TiCl_4 is preferably carried out as gradually as possible, preferably over a period of at least half an hour.

Furthermore it is of importance that the particles of catalyst component D should be comparatively round, smooth granules. Therefore all internal parts of the reactor in which this component is prepared should be cooled to the temperature below -5°C . before the $\text{Al(alkyl)}_2\text{Cl}$ or the TiCl_4 is fed to the reactor, and the presence of aromatic hydrocarbons in the diluent should be avoided as much as

possible. Preferably catalyst component D is prepared by feeding first the $\text{Al(alkyl)}_2\text{Cl}$ to the said reactor and then the TiCl_4 . In the preparation of catalyst component D both the TiCl_4 and the $\text{Al(alkyl)}_2\text{Cl}$ are preferably used in a concentration of more than 500 millimoles per litre of the paraffinic diluent, the most preferred concentration of the $\text{Al(alkyl)}_2\text{Cl}$ being lower than 1800 millimoles per litre of the diluent, however.

Examples of suitable paraffinic diluents are alkanes with 4—10 carbon atoms, such as n-butane, n-pentane, n-hexane, 2,2,4-trimethylpentane, n-decane, isomers of these hydrocarbons, or mixtures of the alkanes mentioned. The presence of an appreciable amount of cycloaliphatic hydrocarbons in the diluent is not very desirable. As diluent also liquid propane or propene can be employed. It is recommendable to ensure that the diluents are dry and substantially free from oxygen, that is, contain less than 250 ppm oxygen.

In the preparation of catalyst component D beside TiCl_4 also $\text{Al(alkyl)}_2\text{Cl}_2$ is formed, which compound is preferably removed from the mixture obtained, for instance by washing with an aliphatic diluent, or converted into $\text{Al(alkyl)}_2\text{Cl}$ (for instance by reaction with Al(alkyl)_3 at a temperature below 20°C ., preferably below 0°C .) or into a complex (for instance by complexing with a Lewis base).

Generally the mixing of the $\text{Al(alkyl)}_2\text{Cl}$ and the TiCl_4 is effected gradually. For this purpose stirring is preferably done with a specific stirring power of 50—2000 W/m^3 , in particular of 80—800 W/m^3 . The stirring power is determined via measurement of the torque of the driving motor and the speed of the stirrer in the way described by J. H. Rushton, E. W. Costich and H. J. Everett in Chem. Eng. Progress 46, (1950), 395—404 and 467—477. The specific stirring power is the stirring power in watts per cubic metre reactor charge. Generally the dimensions of the formed particles of catalyst component D are smaller according as the stirring power is higher. Usually the diameter of these particles will vary between about 6 and about 25 μ ; the most preferred particle size is between 13 and 17 μ .

The increase of the temperature from below -5°C . to 70 — 200°C . is preferably effected as gradually as possible. In this operation a temperature increase of 0.1 — 1.5°C . per minute is preferred as long as the temperature is still below $+45^\circ\text{C}$., while—in addition—it is recommendable to keep the temperature between $+15^\circ\text{C}$. and $+45^\circ\text{C}$. for at least $3/4$ hour and at most 2 hours. The time during which the temperature between 70 and 200°C . is applied may be shorter according as that temperature is higher. When heating is carried out at 150° — 160°C . a heating time as short as 1 hour suffices; when heating is done at 100°C .

this temperature will mostly have to be maintained for at least 20 hours in order to obtain sufficient conversion of beta-TiCl₃ into gamma-TiCl₃.

- 5 After the heating to temperatures between 70 and 200° C. the mixture is usually allowed to cool to temperatures below 70° C., for instance to the ambient temperature.

- 10 Furthermore it is recommendable that the reaction vessel in which the mixing of Al(alkyl)₂Cl and TiCl₄ takes place should not contain any baffles.

- 15 Preferably in this vessel high-speed stirrers are employed which have a sweeping volume of less than 10 per cent of the internal volume of the vessel and which rotate at a peripheral speed (tip speed) of more than 0.5 metre per second. Turbine stirrers are preferred most.

- 20 The organo-metallic catalyst component C is preferably an Al(alkyl)₂Cl. The most suitable ratio of this component to catalyst component D is such that the final Al/Ti atomic ratio is between 0.5:1 and 10:1. The most preferred representative of component C is Al(ethyl)₂Cl.

In the preparation of catalyst component D, too, as Al(alkyl)₂Cl preferably Al(ethyl)₂Cl is used.

- 30 If desired, the polymerizations in the presence of the catalyst components C and D can be carried out while dosing very small amounts of water. As a rule, in that case less than 10, for instance 2—6, parts by weight of water per million parts by weight of diluent is employed.

- 35 The intrinsic viscosity of the polymers A and B, and consequently also the melt index of the final mixture of polymers A and B, can, for example, be controlled by changing the polymerization temperature and/or employing hydrogen. Preferably it is ensured that the intrinsic viscosity of polymer A is between 1.5 and 4 (measured at 135° C. in decalin) and that the melt index of the final mixture of polymers A and B is 0.2—10 (measured at 230° C. according to British Standard 2782, Part I).

- 40 The ethene content of the rubberlike copolymer B and the weight ratio of this polymer to the sum of polymer A and polymer B can be calculated from the material balance. It is also possible to calculate these values with the aid of an infrared analysis, use being made of, inter alia, the peak absorbance at 13.89 microns and the absorbance at 13.62 microns, and calibration being done with samples of which the ethene content is known (for instance samples containing ethene labeled with C¹⁴).

- 45 The present process is excellently suited for the continuous preparation of suspensions in which the desired final polymer is present in a high concentration and from which, by removing the diluent, non-sticking polymer

powders can be obtained which not only have good powder flow properties and a favourable melt index, but can also be processed into products of which the falling-weight impact strength and the yield stress have attractive values. Furthermore the powders usually contain less than 10%w of material that can be extracted with boiling diethyl ether.

The powder flow rate is expressed in seconds per litre and measured in accordance with ASTM—D 1182—54. The falling-weight impact strength is indicated in ft.lb. and measured at 0° C. according to British Standard 2782, Part III.

EXAMPLES

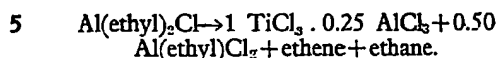
A number of experiments were carried out continuously, in two polymerization reactors connected in series, in the first reactor propene being polymerized at 60° C. to a predominantly isotactic propene homopolymer. The catalyst system consisted of Al(ethyl)₂Cl and a gamma-TiCl₃, the preparation of which is described below in more detail. The intrinsic viscosity of the homopolymer was controlled with the aid of hydrogen. Further reaction conditions are given in Tables A and B below.

The polymer suspension which was formed in the first reactor and which contained still-active catalyst was fed to the second reactor, in which ethene and propene were copolymerized. Further data about the reaction conditions used here are also given in Tables A and B, together with the intrinsic viscosity of the homopolymer and a number of properties of the final product.

The polymer suspension discharged from the second reactor was worked up by successively adding butanol and gaseous hydrogen chloride, extracting three times with water at 50° C., employing three series-connected combinations of equipment, each consisting of a mixer followed by a settler, and—after mixing with 0.05 %w (calculated on polymer) of 1,2,5 - trimethyl - 2,4,6 - tri(3,5-di - tert.butyl - 4 - hydroxybenzyl)benzene and a small amount of Na₂CO₃ (pH about 9), isolating the final product from the organic top layer by removing the diluent with steam, and drying the product thus obtained at 70° C. under nitrogen.

The gamma-TiCl₃ employed as catalyst component D was prepared beforehand in two series-connected premmix reactors, under nitrogen. For this purpose all internal parts of the first premmix reactor were brought to a temperature of -30° C., after which first all the Al(ethyl)₂Cl, cooled to -30° C., was added to this reactor and then the TiCl₄, the temperature of which also was -30° C. During the preparation stirring was carried out continuously with a turbine stirrer with 6 blades, using a specific stirring power of 300 W/m³.

The $\text{Al}(\text{ethyl})_2\text{Cl}$ and the TiCl_4 were mixed in the first premix reactor in a molar ratio corresponding with the reaction equation:
 $1 \text{ TiCl}_4 + 0.75$



The $\text{Al}(\text{ethyl})_2\text{Cl}$ and the TiCl_4 were dissolved beforehand in a hydrocarbon fraction which contained about 33 %w of 2,2,4-trimethylpentane and over 62 %w of other octane isomers, had a boiling range of about 100–112° C. and was virtually free from aromatics water and oxygen. The $\text{Al}(\text{ethyl})_2\text{Cl}$ concentration was about 800 millimoles per litre, the TiCl_4 concentration about 2000 mmole/l. The TiCl_4 was added in 3 hours. During this addition the contents of the reactor were kept at –30 to –35° C. Subsequently, while maintaining the stirring conditions mentioned, the temperature of the first premix reactor was gradually increased to 40° C., after which it was kept at 40° C. for 2 hours.

The reaction product thus obtained was then fed to the second premix reactor, where it was gradually heated from 40 to 160° C., likewise with stirring, after which it was kept at 160° C. for 1 hour and subsequently cooled to room temperature in 1 hour.

During this preparation in both premix reactors a nitrogen-containing gas cap was maintained.

The particle size of the catalyst component D thus prepared was 14–16 microns. In order to free this gamma- TiCl_3 from $\text{Al}(\text{ethyl})\text{Cl}_2$ as much as possible, the product discharged from the second premix reactor was washed twice under nitrogen with dry hydrocarbon fraction mentioned earlier.

In Tables A and B, which relate to the polymerizations and copolymerizations, beside the reaction conditions also the properties of the obtained products are mentioned. Table A concerns the preparation of final products with a melt index of about 0.5–1.0, and Table B the preparation of final products with a melt index of about 2.5–5.

TABLE A

Experiment No.	1	2	3	4
Reaction conditions				
Homopolymerization (continuous)				
Temperature, °C	60	60	60	60
Total pressure, atm.abs.	6	6	6	6
TiCl_3 conc., mmole/l	3.3	3.3	3.3	3.3
$\text{AlEt}_2\text{Cl}/\text{TiCl}_3$ molar ratio	3	3	3	3
Polymer conc. in final suspension, %w	32	31	29	27
Copolymerization (continuous)				
Temperature, °C	68	68	60	60
Total pressure, * atm.abs.	1.9	1.9	1.8	1.8
Molar ratio of $\text{C}_2=/\text{C}_3=$ in gas cap	35/65	35/65	35/65	35/65
Polymer conc. in final suspension, %w	36	35	34	33
Product properties				
Homopolymer				
Intrinsic viscosity, dl/g	3.3	3.3	3.4	4.0
Final product				
Melt index, g/10 min.	0.9	0.9	0.8	0.5
Rubber content, %w	10.0	12.0	13.7	18.6
$\text{C}_2=$ content of the rubber, %w	61	62	60	59
Yield stress, kg/cm ²	300	285	270	240
Falling-weight impact strength at 0°C, ft. lb.	5.0	8.0	8.5	9.5
Ether extract, ** %w	5.5	5.5	5.0	4.5
Powder flow rate, s/l	9.0	8.1	9.0	10.0

* $\text{C}_2= + \text{C}_3= + \text{nitrogen} + \text{vapour}$ from the diluent

** obtained with boiling diethyl ether

TABLE B

Experiment No.	5	6	7	8	9	10	11
Reaction conditions							
Homopolymerization (continuous)							
Temperature, °C	60	60	60	60	60	60	60
Total pressure, atm.abs.	6	6	6	6	6	6	6
TiCl ₃ conc., mmole/l	3	3	3	3	3.3	3	3
AlEt ₂ Cl/TiCl ₃ molar ratio	3	3	3	3	3	3	3
Polymer conc. in final suspension, %w	28	30	27	26	26	30	26
Copolymerization (continuous)							
Temperature, °C	60	60	60	60	75	75	68
Total pressure*, atm.abs.	1.75	1.75	1.75	1.75	2.0	2.0	1.9
Molar ratio of C ₂ =/C ₃ = in gas cap	30/70	30/70	30/70	30/75	35/65	35/65	35/65
Polymer conc. in final suspension, %w	30	33	30	30	30	35	32
Product properties							
Homopolymer							
Intrinsic viscosity, dl/g	2.5	2.6	2.6	2.3	2.7	2.6	2.7
Final product							
Melt index g/10 min.	3.0	3.5	2.5	5.0	2.5	2.8	2.2
Rubber content, %w	7.4	8.4	10.2	12.8	14.0	15.5	18.8
C ₂ = content of the rubber, %w	54	55	55	54	61	57	58
Yield stress, kg/cm ²	300	290	280	275	270	260	235
Falling-weight impact strength at 0°C, ft. lb.	>0.25	1.2	3.3	5	6	6	8
Ether extract**, %w	5.8	7.9	7.8	6.1	8	7.6	7.3
Powder flow rate, s/l	10.0	11.0	10.2	10.9	10.5	8.2	13.4

* see note under Table A

** do.

WHAT WE CLAIM IS:—

1. A process for the preparation of polypropene compositions in the form of a powder, which contain a predominantly isotactic propene polymer (polymer A) and a rubber-like ethene-propene copolymer (polymer B), which may or may not be bound to polymer A, by the following procedure, to be carried out in the presence of a liquid diluent: (a) polymerizing propene to a suspension of polymer A; (b) copolymerizing ethene and propene to a suspension containing polymer B; and (c) mixing the polymers A and B during or after the copolymerization mentioned under (b); and subsequently removing the diluent from the final suspension thus obtained, in which process:

(1) the preparation of the suspension of polymer A is carried out with the aid of a catalyst system consisting of an organometallic component C and a component D which has been prepared beforehand by mixing, in liquid paraffinic diluent and with stirring, Al(alkyl)₂Cl and TiCl₄ at a temperature below -5° C. and in a molar ratio of 0.5—1.2 and subsequently raising the temperature of the mixture thus obtained to 70—200° C., with continued stirring;

(2) the intrinsic viscosity of polymer A, measured in decalin at 135° C., is 1—4.5 dl/g;

(3) polymer B contains 20—90 per cent by weight of copolymerized ethene;

(4) in the final suspension the weight ratio between polymer B and the sum of polymer A and polymer B is 0.08—0.20;

(5) the melt index of the final mixture of polymer A and polymer B is 0.1—15.0, measured at 230° C. according to British Standard 2782, Part I.

2. A process as claimed in Claim 1 in which in the preparation of the suspension of polymer A the polymerization is continued until a polymer concentration of more than 25 per cent by weight is reached.

3. A process as claimed in Claim 1 or 2, in which the polymer concentration in the final suspension, before removal of the diluent is 30—37 per cent by weight.

4. A process as claimed in any one of Claims 1—3, in which in the final suspension the polymer B/polymer A+polymer B weight ratio of 0.08—0.20 is realized by carrying out the preparation of polymer B in the presence of a polymer-A suspension which contains still-active catalyst.

5. A process as claimed in Claim 4, in

- which the polymerization to polymer A and the copolymerization to polymer B are carried out continuously in separate reactors, the suspension obtained at the end of the preparation of polymer A—which suspension contains still-active catalyst—being fed to a reactor in which polymer B is prepared.
6. A process as claimed in any one of Claims 1—5, in which in the preparation of catalyst component D the $\text{Al(alkyl)}_2\text{Cl}$ and the TiCl_4 are mixed at a temperature above -45°C ., the mixing being carried out gradually over a period of at least half an hour.
7. A process as claimed in any one of Claims 1—6, in which in the preparation of catalyst component D the mixing of $\text{Al(alkyl)}_2\text{Cl}$ and TiCl_4 was started at a temperature between -10 and -40°C .
8. A process as claimed in any one of Claims 1—7, in which in the preparation of catalyst component D all internal parts of the reactor in which this preparation was carried out were cooled to a temperature below -5°C . before the $\text{Al(alkyl)}_2\text{Cl}$ or the TiCl_4 were fed to that reactor.
9. A process as claimed in any one of Claims 1—8, in which in the preparation of catalyst component D first the $\text{Al(alkyl)}_2\text{Cl}$ and then the TiCl_4 was fed to the reactor used for the preparation.
10. A process as claimed in any one of Claims 1—9, in which in the preparation of catalyst component D the molar ratio in which the $\text{Al(alkyl)}_2\text{Cl}$ and the TiCl_4 were mixed was 0.65—1.00.
11. A process as claimed in any one of Claims 1—10, in which in the preparation of catalyst component D both the TiCl_4 and the $\text{Al(alkyl)}_2\text{Cl}$ were used in a concentration of more than 500 millimoles per litre of the paraffinic diluent.
12. A process as claimed in Claim 11, in which the $\text{Al(alkyl)}_2\text{Cl}$ concentration was lower than 1800 millimoles per litre of the paraffinic diluent.
13. A process as claimed in any one of Claims 1—12, in which in the preparation of catalyst component D the $\text{Al(alkyl)}_2\text{Cl}_2$ also formed during this preparation was removed from the mixture obtained or converted into $\text{Al(alkyl)}_2\text{Cl}$ or into a complex.
14. A process as claimed in any one of Claims 1—13, in which in the preparation of catalyst component D stirring was carried out with a specific stirring power of at least 50 W/m^3 .
15. A process as claimed in any one of Claims 1—14, in which as catalyst component C $\text{Al(alkyl)}_2\text{Cl}$ is used.
16. A process as claimed in Claim 15, in which as catalyst component C $\text{Al(ethyl)}_2\text{Cl}$ is used and in which also in the preparation of catalyst component D $\text{Al(ethyl)}_2\text{Cl}$ was used as $\text{Al(alkyl)}_2\text{Cl}$.
17. A process as claimed in any one of Claims 1—16, in which polymer B contains 40—70 per cent by weight of copolymerized ethene.
18. A process as claimed in Claim 17, in which polymer B contains 50—65 per cent by weight of copolymerized ethene.
19. A process as claimed in any one of Claims 1—18, in which in the final suspension the weight ratio between polymer B and the sum of polymer A and polymer B is 0.11—0.15.
20. A process as claimed in any one of Claims 1—19, in which the intrinsic viscosity of polymer A is 1.5—4 and the melt index of the final mixture of polymer A and polymer B 0.2—10.0.
21. A process as claimed in Claim 1 substantially as described hereinbefore with special reference to the Examples.
22. Polypropene compositions in the form of a powder whenever obtained by a process as claimed in any one of claims 1—21.
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